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(54) **Silver halide photographic material having antistatic properties**

(57) The present invention relates to a silver halide photographic material comprising a support, at least one silver halide emulsion layer coated thereon, and a hydrophilic colloid layer coated on said at least one silver halide emulsion layer, wherein said hydrophilic colloid layer comprises a combination of (a) at least one surfactant selected from the group consisting of non-ionic perfluoroalkyl(ene)-polyoxyethylene surfactants and polyoxyethylene-modified polysiloxane surfactants, and (b) at least one salt of perfluoroalkylsulfonyl imide or perfluoroalkylsulfonyl methide.

**EP 0 690 338 A1**

## Description

## FIELD OF THE INVENTION

5 The present invention relates to a silver halide photographic material, more particularly to a silver halide photographic material having improved antistatic property and improved coating ability.

## BACKGROUND OF THE INVENTION

10 Silver halide photographic materials are generally composed of an electrically insulating support and photographic layers coated thereon. Such a structure promotes the formation and accumulation of static charges when subjecting the photographic materials to friction or separation, caused by contact with the surface of the same or different materials during steps for manufacturing of the photographic materials or when using them for photographic purposes. These accumulated static charges cause several drawbacks. The most serious drawback is discharge of accumulated charges  
15 prior to development processing, by which the light-sensitive silver halide emulsion layer is exposed to light to form dot, spots, or branched or feathery linear specks when development of the photographic film is carried out. This phenomenon is called "static marks". Such static marks cause a reduction of the commercial value of photographic films, which sometimes become useless. For example, the formation of static marks in medical or industrial X-ray films may result in a very dangerous judgment or erroneous diagnosis. Static marks are a particular problem because it becomes evident  
20 for the first time after development. Further, these static charges are also the origin of secondary problems such as adhesion of dust to the surface of films, uneven coating, and the like.

As mentioned above, static charge is frequently accumulated when manufacturing and/or using silver halide photographic materials. For example, during production, they are generated by friction of the photographic film contacting a roller or by separation of the emulsion surface from a support surface during a rolling or unrolling step. Further, they  
25 are generated on X-ray films in an automatic apparatus by contact with or separation from mechanical parts or fluorescent screens, or they are generated by contact with or separation from rollers and bars made of rubber, metal, or plastics in a bonding machine or an automatic developing machine or an automatic developing apparatus or in a camera in the case of color negative films or color reversal films. In addition they can be generated by contact with packing materials, and the like.

30 Silver halide photographic materials having high sensitivity and handling speed are subject to an increase of static mark appearance. In particular, static marks are easily generated because of high sensitization of the photographic material and severe handling conditions such as high speed coating, high speed exposure, and high speed automatic processing.

To prevent problems caused by static charges, it is suitable to add an antistatic agent to the silver halide photographic materials. However, antistatic agents conventionally used in other fields cannot be used universally for silver halide photographic materials, because they are subjected to various restrictions due to the nature of the photographic materials. More specifically, the antistatic agents which can be used in silver halide photographic materials must have excellent antistatic abilities while not having adverse influences upon photographic properties of the photographic materials, such as sensitivity, fog, granularity, and sharpness. Such antistatic agents also must not have adverse influences upon the  
40 film strength and upon antiadhesion properties. Furthermore, the antistatic agents must not accelerate exhaustion of processing solutions and not deteriorate adhesive strength between layers composing the silver halide photographic material.

In the art of silver halide photographic materials, a wide number of solutions to the above described problems have been suggested in patent and literature references, mainly based on charge control agents and electrically conductive compounds coated on the silver halide emulsion layer together with a binder as an antistatic layer.  
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The most useful charge control agents known in the art are ionic and non-ionic surfactants as well as ionic salts. Fluorinated surfactants are often mentioned as good antistatic agents in silver halide photographic materials.

Electrically conductive compounds are mainly focused on conductive polymers such as ionic polymers and electronically conductive polymers.

50 The use of ionic and non-ionic surfactants as well as fluorinated surfactants is widely disclosed in many patents, such as, for example, US 2,600,831, 2,719,087, 2,982,651, 3,026,202, 3,428,456, 3,457,076, 3,454,625, 3,552,972, 3,655,387, 3,850,640, 3,850,642, 4,192,683, 4,267,265, 4,304,852, 4,330,618, 4,367,283, 4,474,873, 4,510,233, 4,518,354, 4,596,766, 4,649,102, 4,703,000, 4,847,186, 4,891,307, 4,891,308, 4,916,054, EP 245,090, 300,259, 319,951, 370,404, and the like.

55 The use of conductive polymers is widely disclosed in many other patents, such as, for example, US 2,882,157, 2,972,535, 3,062,785, 3,262,807, 3,514,291, 3,615,531, 3,753,716, 3,769,020, 3,791,831, 3,861,924, 3,938,999, 4,147,550, 4,225,665, 4,363,872, 4,388,402, 4,460,679, 4,582,783, 4,585,730, 4,590,151, 4,701,403, 4,960,687, EP 35,614, 36,702, 87,688, 391,176, 391,402, 424,010, GB 815,662, 1,222,595, 1,539,866, 2,001,078, 2,109,705.

In particular, US 4,272,615 discloses the use of a non-ionic perfluoroalkenylpolyoxyethylene surfactant, US 4,649,102 discloses the combination of a non-ionic surfactant and an anionic surfactant having a polyoxyethylene group therein, US 4,847,186 discloses the use of a fluorinated ionic or non-ionic compound, EP 245,090 discloses the combination of fluoroalkylpolyoxyethylene compounds with fluorine-containing polymers and a polyoxyethylene non-ionic surfactant together with a high-molecular high weight hardening agent, US 3,850,640 discloses the combination of a first layer comprising an anionic surfactant and a second layer comprising cationic and non-ionic surfactants, US 4,596,766 discloses the combination of a polyoxyethylene non-ionic surfactant and a fluorine-containing compound, US 4,367,283 discloses the combination of a polyoxyethylene non-ionic surfactant, a sulfonated surfactant, and a fluorine-containing phosphate surfactant, US 4,335,201 discloses the use anionic fluoroalkyl surfactant, such as fluoroalkyl sulfonate, sulfate and carboxylate salts, GB 2,246,870 discloses the combination of a polyoxyalkylene compound and a polystyrenesulfonate compound, US 5,037,871 and WO 91/18325 disclose the use of hydrolyzed metal lower alkoxide in combination with fluoroalkyl polyether surfactants and a water-soluble hydroxylated polymer, US 4,891,308 discloses the use of ionic and non-ionic fluorine containing surfactant together with a fluorine free non-ionic surfactant, EP 319,951 describes the combination of an anionic and non-ionic surfactant with a fluorinated non-ionic surfactant, US 4,610,955 and 4,582,781 describe the combination of an inorganic salt with polymers containing blocks of polymerized oxyalkylene monomers, US 5,176,943 discloses an antistatic composition comprising an ionic perfluoro surfactant, a nonionic perfluoro surfactant and a nonfluorinated, copolymerizable, radiation curable prepolymer, US 5,258,276 discloses a ternary surfactant system comprising a mixture of a specific anionic and two specific nonionic surfactants.

However, many of these substances and combinations thereof exhibit great specificity, depending upon the kind of film support or the photographic composition. Although some substances produce good results on certain specific film supports, photographic emulsions or other photographic elements, they are not only useless for preventing generation of static marks when using different film supports and photographic elements, but also may have an adverse influence upon photographic properties.

On the other hand, there are many cases wherein, although they have excellent antistatic effects, they cannot be used due to their adverse influence upon photographic properties such as sensitivity, fog, granularity, sharpness, and the like.

For example, it has been well known that polyethylene oxide compounds have antistatic effects, but they often have an adverse influence upon photographic properties, such as an increase in fog, desensitization, and deterioration of granularity, in particular in silver halide photographic materials in which both sides of the support are coated with silver halide emulsions, such as medical X-ray photographic materials. The combination of polyoxyethylene compounds with organic salts can improve the surface resistivity, but also may increase of tackiness and film-to-film adhesion.

The use of fluorinated surfactants for controlling the electricity generation caused by friction or contacting with different materials, such as, for example, rollers, increases the charging in negative polarity. Accordingly, although it is possible to adapt the electric characteristics of the silver halide photographic material for each roller, such as, for example, rubber rollers, Delrin™ rollers, and nylon rollers by suitably combining the fluorinated surfactants with surfactants, charging in positive polarity problems still occurs, because a general solution for all kind of rollers cannot be obtained.

Moreover, the market requirement of silver halide photographic material having a reduced processing time has increased the problems of static charges due to the higher speed to which silver halide photographic materials go through the automatic processors.

Furthermore, the increasing demand of the radiographic market of medical X-ray silver halide photographic material, due to the increase in the worldwide consumption and diffusion of apparatus for X-ray diagnosis, requires an increase in productivity of medical X-ray photographic material that can be obtained with an increase of coating speed. Higher coating speed increases the likelihood of static charges if conventional antistatic agents are used.

## SUMMARY OF THE INVENTION

The present invention relates to a silver halide photographic material comprising a support, at least one silver halide emulsion layer coated thereon, and a hydrophilic colloid layer coated on said at least one silver halide emulsion layer, wherein said hydrophilic colloid layer comprises a combination of (a) at least one surfactant selected from the group consisting of non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants and polyoxyethylene-modified polysiloxane surfactants, and (b) at least one salt selected from the group of salts of perfluoroalkylsulfonate or perfluoroalkylsulfonate methide.

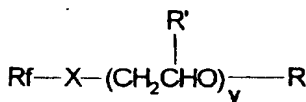
## DETAILED DESCRIPTION OF THE INVENTION

The silver halide photographic material according to the present invention comprises a combination of a non-ionic perfluoroalkyl(ene)polyoxyethylene surfactant and/or a polyoxyethylene-modified polysiloxane surfactant, and at least one salt of a perfluoroalkylsulfonate or perfluoroalkylsulfonate methide. The combination is coated on the silver halide emulsion layer together with a hydrophilic binder as a top-coat protective layer.

The term "non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants" means a non-ionic surfactant comprising a mixture of compounds consisting in an alkyl or alkylene group of from 4 to 16 carbon atoms wherein the hydrogens are totally replaced by fluorine atoms (at least 90% of the hydrogens are replaced by fluorine) joined to a polyoxyethylene group comprising from 6 to 30 oxyethylene groups.

According to the scope of the present invention when the term "group" is used to describe a chemical compound or substituent, the described chemical material includes the basic group and that group with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent only an unsubstituted chemical material is intended to be included.

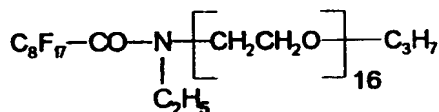
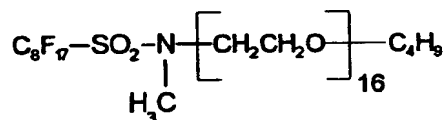
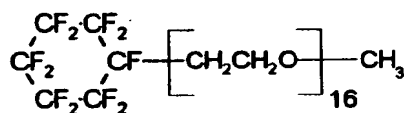
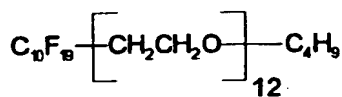
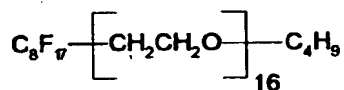
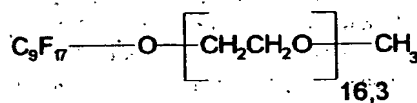
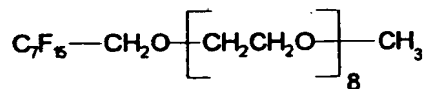
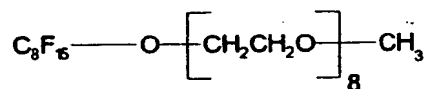
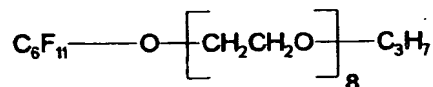
The non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants can be represented by the following formula:

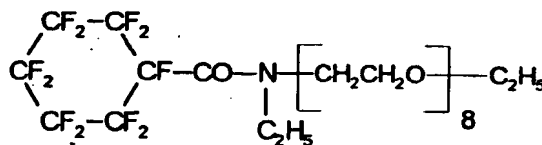
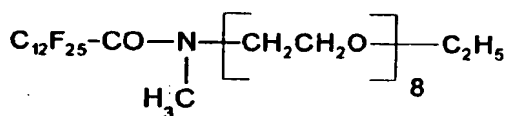


wherein Rf can be a perfluoroalkyl group, a perfluoroalkylene group, a perfluorocycloalkyl group, and a perfluorocycloalkylene group having from 4 to 16 carbon atoms, X can be -O-, -SO<sub>2</sub>NR'', -CONR'', -CH<sub>2</sub>O-, or a single bond, R, R' and R'' are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms, and y is a number from 6 to 30.

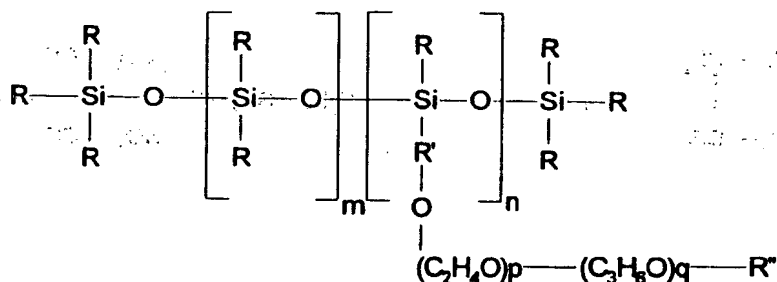
A particularly preferred non-ionic perfluoroalkylpolyoxyethylene surfactant is the Zonyl™ FSN, a trade name of DuPont Company. Non-ionic perfluoroalkyl(ene)polyoxyethylene surfactants are used in amount of from 10 to 100 mg/m<sup>2</sup>, preferably from 20 to 60 mg/m<sup>2</sup>, more preferably of about 40 mg/m<sup>2</sup> of top-coat protective layer. Other useful non-ionic

perfluoroalkyl(ene)poly-oxyethylene surfactants are listed below.



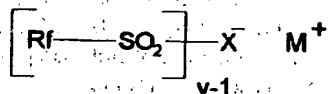


The polyoxyethylene-modified polysiloxane surfactant comprises a non-ionic polysiloxane polymer (preferably having a linear polymeric backbone) which has pendant polyoxyethylene polymeric units adhered to the polysiloxane backbone. The polyoxyethylene chain is preferably linked to the polysiloxane through ether linkages, and the polyoxyethylene may also contain propylene units as random or block units throughout the polyoxyethylene chain. The polyoxyethylene-modified polysiloxane surfactant can be better represented by the following formula:



wherein R is a lower alkyl having from 1 to 4 carbon atoms, R' is a lower alkylene having from 1 to 4 carbon atoms, R'' is hydrogen or a lower alkyl of from 1 to 4 carbon atoms, m is an integer from 5 to 100, n is an integer from 2 to 50, p is an integer from 5 to 50, and q is an integer from 0 to 50. Compounds of this class are sold by Union Carbide Co., under the trade name of Silwet™. Examples of useful compounds for use in the combination of the present invention are Silwet™ L-7605, Silwet™ L-77, Silwet™ L-7001, and the like. The polyoxyethylene-modified polysiloxane surfactants are used in amount of from 1 to 100 mg/m<sup>2</sup>, preferably from 5 to 50 mg/m<sup>2</sup> of top-coat protective layer.

The salt of perfluoroalkylsulfonyl imide or perfluoroalkylsulfonyl methide useful in the combination of the present invention can be represented by the following formula:



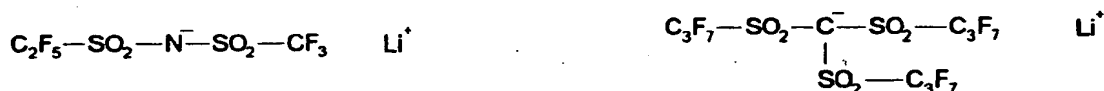
wherein Rf is a fluorinated alkyl group having 1 to 10 carbon atoms, X is nitrogen or carbon atom, M is an organic or inorganic cation, and v is the X valence, and wherein two Rf groups can join together to form a ring.

In a preferred embodiment M can be any of alkali metal cations, alkaline-earth metal cations, an alkyl ammonium cation, or a quaternary ammonium cation. In a more preferred embodiment M can be Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>. In the most preferred embodiment M is Li<sup>+</sup>.

In a preferred embodiment, v is 3 when X is nitrogen atom, and v is 4 when X is a carbon atom.

A description of the above mentioned compounds and their synthesis can be found in US 4,505,997, US 5,021,308, US 5,072,040, US 5,162,177 and 5,273,840, incorporated herein by reference. Examples of lithium salts of perfluoroalkylsulfonyl imide or perfluoroalkylsulfonyl methide are illustrated below. However, the present invention is not limited

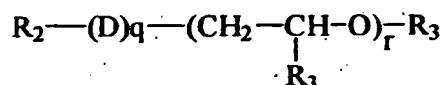
to the following examples.



The salts of perfluoroalkylsulfonyl imides or perfluoroalkylsulfonyl methides are employed in an amount of from 1 to 100 mg/m<sup>2</sup>, preferably from 5 to 80 mg/m<sup>2</sup>, more preferably from 10 to 70 mg/m<sup>2</sup> of top-coat protective layer.

The top-coat layer comprising the antistatic combination of the present invention can comprise other compounds conventionally known in the art, such as, for example, coating aids, hardeners, and the like. Particularly useful coating aids are ionic and non-ionic polyoxyethylene surfactants and alkylsulfate surfactants. The antistatic layer of the present invention may contain other addenda which do not influence the antistatic properties of the layer, such as, for example, matting agents, plasticizers, lubricants, dyes, and haze reducing agents.

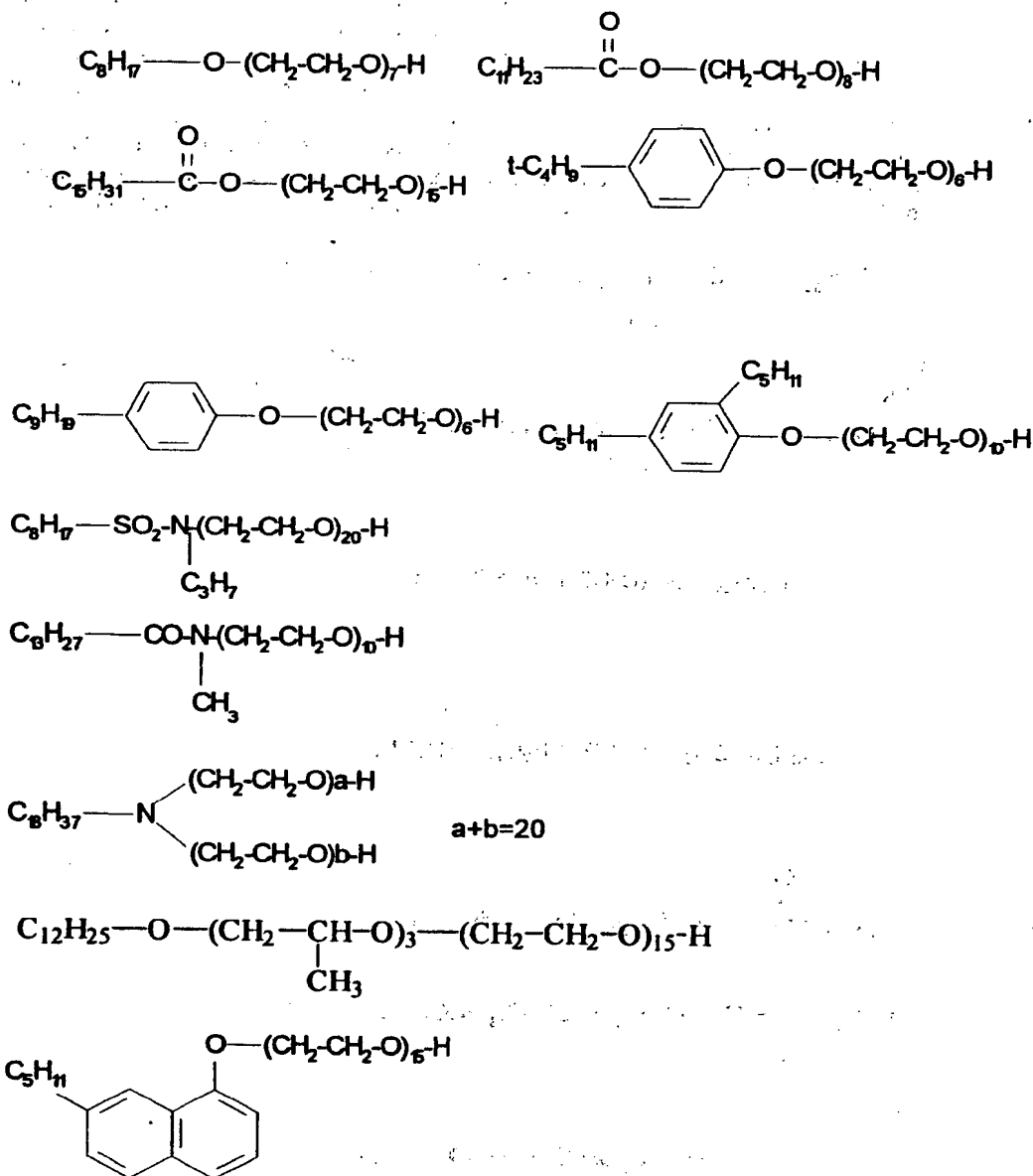
More particularly, the non-ionic polyoxyethylene surfactants useful as coating aids in the top-coat layer comprising the combination of the present invention can be represented by the following formula:



wherein R<sub>2</sub> represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 1 to 30 carbon atoms or an aryl group having 6 to 30 ring atoms (such as phenyl or naphthyl) or a combination thereof, R<sub>3</sub> represents a hydrogen

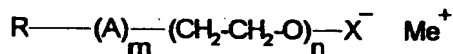
atom or a methyl group, D represents a group  $-O-$ ,  $-S-$ ,  $-COO-$ ,  $-NR_4-$ ,  $-CO-NR_4-$ , or  $-SO_2-NR_4-$ , wherein  $R_4$  represents a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, q represents 0 or 1 and r represents an integer of 2 to 50.

Examples of non-ionic polyoxyalkylene surfactants are illustrated below.



The non-ionic polyoxyalkylene surfactants are employed in an amount of from 10 to 200 mg/m<sup>2</sup>, preferably from 20 to 150 mg/m<sup>2</sup>, more preferably from 30 to 120 mg/m<sup>2</sup> of top-coat protective layer.

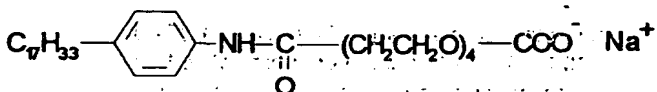
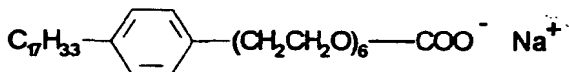
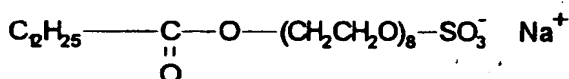
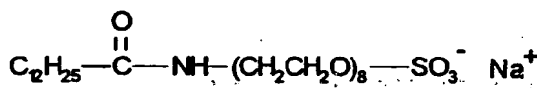
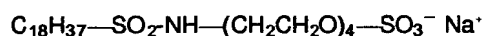
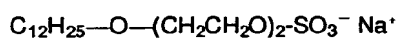
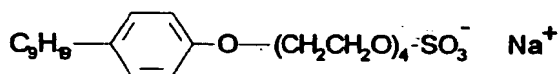
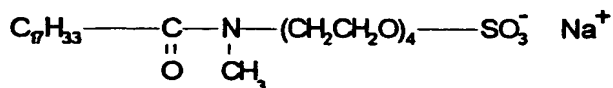
Anionic polyoxyethylene surfactants, normally used in photography, are surfactants of the type including a polyoxyethylene group linked to an anionic hydrophilic group and to a hydrocarbon residue directly or by means of a bridge consisting of a divalent organic residue, as expressed by the following formula:





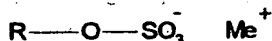
wherein R is an aliphatic, aromatic or a mixed hydrocarbon residue and preferably a linear or branched alkyl group having from 4 to 18 carbon atoms or an aryl group substituted with one or more alkyl groups altogether having from 4 to 18 carbon atoms, A is a divalent organic residue, preferably a carbonyl, a sulfonyl, an amino or an alkylene group preferably having from 1 to 3 carbon atoms, an oxygen atom or groups consisting of two or more of the above-mentioned groups, such as for example carbonylamino, sulfonylamino, aminocarbonyl, aminosulfonyl, or ester, X is an anionic group selected from the class consisting of sulfonate group, carboxylate group, phosphate group and sulfate group,

Me is an alkaline or alkaline-earth metal, such as Na, K, Li, Ca, Mg, and the like, and m is 0 or 1 and n is an integer of from 1 to 25. Anionic surface active agents of this type are described for example in Schwarz et al. "Surface Active Agents and Detergents", Vol. I and II, Interscience Publ., in the US Pat. Nos. 2,992,108, 3,068,101, 3,201,152 and 3,165,409, in the French Pat. Nos. 1,556,240 and 1,497,930 and in the British Pat. Nos. 580,504 and 985,483. Examples of anionic polyoxyethylene surfactants useful in the combination of the present invention are listed hereinbelow.



The anionic polyoxyalkylene surfactants are employed in an amount of from 10 to 200 mg/m<sup>2</sup>, preferably from 20 to 100 mg/m<sup>2</sup>, more preferably from 30 to 80 mg/m<sup>2</sup> of top-coat protective layer.

Alkylsulfate surfactants, normally used in photography, are surfactants of the type including an alkyl group linked to a sulfate group through an oxygen atom, as expressed by the following formula:



wherein R is an aliphatic group and preferably a linear or branched alkyl group having from 4 to 18 carbon atoms, and Me is an alkali metal, such as Na, K, Li.

The alkylsulfate surfactants are employed in an amount of from 10 to 200 mg/m<sup>2</sup>, preferably from 10 to 100 mg/m<sup>2</sup>, more preferably from 10 to 50 mg/m<sup>2</sup> of top-coat protective layer.

Photographic materials according to the invention generally comprise at least one light sensitive layer, such as a silver halide emulsion layer, coated on at least one side of a support. Silver halide emulsions typically comprise silver halide grains which may have different crystal forms and sizes, such as, for example, cubic grains, octahedral grains, tabular grains, spherical grains and the like. Tabular grains are preferred. The tabular silver halide grains contained in the silver halide emulsion layers of this invention have an average diameter:thickness ratio (often referred to in the art as aspect ratio) of at least 3:1, preferably 3:1 to 20:1, more preferably 3:1 to 14:1, and most preferably 3:1 to 8:1. Average diameters of the tabular silver halide grains suitable for use in this invention range from about 0.3 to about 5 μm, preferably 0.5 to 3 μm, more preferably 0.8 to 1.5 μm. The tabular silver halide grains suitable for use in this invention have a thickness of less than 0.4 μm, preferably less than 0.3 μm and more preferably less than 0.2 μm. The tabular silver halide grain characteristics described above can be readily ascertained by procedures well known to those skilled in the art. The term "diameter" is defined as the diameter of a circle having an area equal to the projected area of the grain. The term "thickness" means the distance between two substantially parallel main planes constituting the tabular silver halide grains. From the measure of diameter and thickness of each grain the diameter:thickness ratio of each grain can be calculated, and the diameter:thickness ratios of all tabular grains can be averaged to obtain their average diameter:thickness ratio. By this definition the average diameter:thickness ratio is the average of individual tabular grain diameter:thickness ratios. In practice, it is simpler to obtain an average diameter and an average thickness of the tabular grains and to calculate the average diameter:thickness ratio as the ratio of these two averages. Whatever the used method may be, the average diameter:thickness ratios obtained do not greatly differ. In the silver halide emulsion layer containing tabular silver halide grains of the invention, at least 15%, preferably at least 25%, and, more preferably, at least 50% of the silver halide grains are tabular grains having an average diameter:thickness ratio of not less than 3:1. Each of the above proportions, "15%", "25%" and "50%" means the proportion of the total projected area of the tabular grains having a diameter:thickness ratio of at least 3:1 and a thickness lower than 0.4 μm, as compared to the projected area of all of the silver halide grains in the layer. Other conventional silver halide grain structures such as cubic, orthorhombic, tetrahedral, etc. may make up the remainder of the grains. In the present invention, commonly employed halogen compositions of the silver halide grains can be used. Typical silver halides include silver chloride, silver bromide, silver iodide, silver chloriodide, silver bromiodide, silver chloro-bromiodide and the like. However, silver bromide and silver bromiodide are preferred silver halide compositions for tabular silver halide grains with silver bromiodide compositions containing from 0 to 10 mol% silver iodide, preferably from 0.2 to 5 mol% silver iodide, and more preferably from 0.5 to 1.5% mol silver iodide. The halogen composition of individual grains may be homogeneous or heterogeneous. Silver halide emulsions containing tabular silver halide grains can be prepared by various processes known for the preparation of photographic materials. Silver halide emulsions can be prepared by the acid process, neutral process or ammonia process. In the stage for the preparation, a soluble silver salt and a halogen salt can be reacted in accordance with the single jet process, double jet process, reverse mixing process or a combination process by adjusting the conditions in the grain formation, such as pH, pAg, temperature, form and scale of the reaction vessel, and the reaction method. A silver halide solvent, such as ammonia, thioethers, thioureas, etc., may be used, if desired, for controlling grain size, form of the grains, particle size distribution of the grains, and the grain-growth rate. Preparation of silver halide emulsions containing tabular silver halide grains is described, for example, in de Cugnac and Chateau, "Evolution of the Morphology of Silver Bromide Crystals During Physical Ripening", *Science and Industries Photographiques*, Vol. 33, No. 2 (1962), pp. 121-125, in Gutoff, "Nucleation and Growth Rates During the Precipitation of Silver Halide Photographic Emulsions", *Photographic Science and Engineering*, Vol. 14, No. 4 (1970), pp. 248-257, in Berry et al., "Effects of Environment on the Growth of Silver Bromide Microcrystals", Vol. 5, No. 6 (1961), pp. 332-336, in US Pat. Nos. 4,063,951; 4,067,739; 4,184,878; 4,434,226; 4,414,310; 4,386,156; 4,414,306 and in EP Pat. Appl. No. 263,508. As a binder for silver halide emulsions and other hydrophilic colloid layers, gelatin is preferred, but other hydrophilic colloids can be used, alone or in combination, such as, for example, dextran, cellulose derivatives (e.g., hydroxyethylcellulose, carboxymethyl cellulose), collagen derivatives, colloidal albumin or casein, polysaccharides, synthetic hydrophilic polymers (e.g., polyvinylpyrrolidone, polyacrylamide, polyvinylalcohol, polyvinylpyrazole) and the like. Gelatin derivatives, such as, for example, highly deionized gelatin, acetylated gelatin and phthalated gelatin can also be used. Highly deionized gelatin is characterized

by a higher deionization with respect to the commonly used photographic gelatins. Preferably, highly deionized gelatin is almost completely deionized which is defined as meaning that it presents less than 50 ppm (parts per million) of  $\text{Ca}^{++}$  ions and is practically free (less than 5 parts per million) of other ions such as chlorides, phosphates, sulfates and nitrates, compared with commonly used photographic gelatins having up to 5,000 ppm of  $\text{Ca}^{++}$  ions and the significant presence of other ions. The amount of gelatin employed in the light-sensitive photographic material of the present invention is such as to provide a total silver to gelatin ratio lower than 1 (expressed as grams of Ag/grams of gelatin). In particular the silver to gelatin ratio of the silver halide emulsion layers is in the range of from 1 to 1.5. Silver halide emulsion layers can be sensitized to a particular range of wavelengths with a sensitizing dye. Typical sensitizing dyes include cyanine, hemicyanine, merocyanine, oxonols, hemioxonols, styryls, merostyryls and streptocyanines. The silver halide photographic material of the present invention can have one or more silver halide emulsion layers sensitized to the same or different regions of the electromagnetic spectrum. The silver halide emulsion layers can be coated on one side or on both side of a support base.

Examples of materials suitable for the preparation of the support include glass, paper, polyethylene-coated paper, metals, polymeric film such as cellulose nitrate, cellulose acetate, polystyrene, polyethylene terephthalate, polyethylene, polypropylene and the like. Specific photographic materials according to the invention are black-and-white light-sensitive photographic materials, in particular X-ray light-sensitive materials. Preferred light-sensitive silver halide photographic materials according to this invention are radiographic light-sensitive materials employed in X-ray imaging comprising a silver halide emulsion layer(s) coated on one surface, preferably on both surfaces of a support, preferably a polyethylene terephthalate support. Preferably, the silver halide emulsions are coated on the support at a total silver coverage in the range of 3 to 6 grams per square meter. Usually, the radiographic light-sensitive materials are associated with intensifying screens so as to be exposed to radiation emitted by said screens. The screens are made of relatively thick phosphor layers which transform the X-rays into more imaging-effective radiation such as light (e.g., visible light). The screens absorb a much larger portion of X-rays than the light-sensitive materials do and are used to reduce the X-ray dose necessary to obtain a useful image. According to their chemical composition, the phosphors can emit radiation in the ultraviolet, blue, green or red region of the visible spectrum and the silver halide emulsions are sensitized to the wavelength region of the radiation emitted by the screens. Sensitization is performed by using spectral sensitizing dyes absorbed on the surface of the silver halide grains as known in the art. More preferred light-sensitive silver halide photographic materials according to this invention are radiographic light-sensitive materials which employ intermediate diameter:thickness ratio tabular grain silver halide emulsions, as disclosed in US 4,425,426 and in EP Pat. Appl. 84,637.

However other black-and-white photographic materials, such as lithographic light-sensitive materials, black-and-white photographic printing papers, black-and-white negative films, as well as light-sensitive photographic color materials such as color negative films, color reversal films, color papers, etc. can benefit of the use of the present invention. The light sensitive layers intended for use in color photographic material contain or have associated therewith dye-forming compounds or couplers. For example, a red-sensitive emulsion would generally have a cyan coupler associated therewith, a green-sensitive emulsion would generally have a magenta coupler associated therewith, and a blue-sensitive emulsion would generally have a yellow coupler associated therewith. The silver halide photographic materials of the present invention are fore-hardened. Typical examples of organic or inorganic hardeners include chrome salts (e.g., chrome alum, chromium acetate), aldehydes (e.g., formaldehyde and glutaraldehyde), isocyanate compounds (hexamethylene diisocyanate), active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-s-triazine), epoxy compounds (e.g., tetramethylene glycol diglycidylether), N-methylol derivatives (e.g., dimethylolurea, methyloldimethyl hydantoin), aziridines, mucohalogeno acids (e.g., mucochloric acid), active vinyl derivatives (e.g., vinylsulfonyl arid hydroxy substituted vinylsulfonyl derivatives) and the like. Other references to well known hardeners can be found in *Research Disclosure*, December 1989, Vol. 308, Item 308119, Section X. Other layers and additives, such as subbing layers, surfactants, filter dyes, intermediate layers, protective layers, anti-halation layers, barrier layers, development inhibiting compounds, speed-increasing agent, stabilizers, plasticizer, chemical sensitizer, UV absorbers and the like can be present in the photographic element. A detailed description of photographic elements and of various layers and additives can be found in *Research Disclosure* 17643 December 1978, 18431 August 1979, 18716 November 1979, 22534 January 1983, and 308119 December 1989. The silver halide photographic material of the present invention can be exposed and processed by any conventional processing technique. Any known developing agent can be used into the developer, such as, for example, dihydroxybenzenes (e.g., hydroquinone), pyrazolidones (1-phenyl-3-pyrazolidone-4,4-dimethyl-1-phenyl-3-pyrazolidone), and aminophenols (e.g., N-methyl-p-aminophenol), alone or in combinations thereof. Preferably the silver halide photographic materials are developed in a developer comprising dihydroxy-benzenes as the main developing agent, and pyrazolidones and p-aminophenols as auxiliary developing agents. Other well known additives can be present in the developer, such as, for example, antifoggants (e.g., benzotriazoles, indazoles, tetrazoles), silver halide solvents (e.g., thiosulfates, thiocyanates), sequestering agents (e.g., aminopolycarboxylic acids, aminopolyphosphonic acids), sulfite antioxidants, buffers, restrainers, hardeners, contrast promoting agents, surfactants, and the like. Inorganic alkaline agents, such as KOH, NaOH, and LiOH are added to the developer composition to obtain the desired pH which is usually higher than 10. The silver halide photographic material of the present invention can be processed with a fixer of typical composition. The fixing agents include thiosulfates, thiocyanates, sulfites, ammonium salts, and the like. The fixer

composition can comprise other well known additives, such as, for example, acid compounds (e.g., metabisulfates), buffers (e.g., carbonic acid, acetic acid), hardeners (e.g., aluminum salts), tone improving agents, and the like. The present invention is particularly intended and effective for high temperature, accelerated processing with automatic processors where the photographic element is transported automatically and at constant speed from one processing unit to another by means of roller. Typical examples of said automatic processors are 3M TRIMATIC™ XP515 and KODAK RP X-OMAT™. The processing temperature ranges from 20° to 60°C, preferably from 30° to 50°C and the processing time is lower than 90 seconds, preferably lower than 45 seconds. The good antistatic and surface characteristics of the silver halide photographic material of the present invention allow the rapid processing of the material without having the undesirable appearance of static marks or scratches on the surface of the film. The invention will be described hereinafter by reference to the following example.

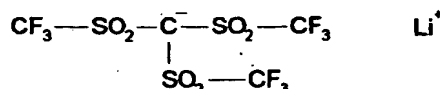
#### EXAMPLE 1

A tabular grain silver bromide emulsion (having an average dia-meter:thickness ratio of about 7.6:1, prepared in the presence of a deionized gelatin having a viscosity at 60°C in water at 6.67% w/w of 4.6 mPas, a conductivity at 40°C in water at 6.67% w/w of less than 150  $\mu$ S/cm and less than 50 ppm of Ca<sup>++</sup>) was optically sensitized to green light with a cyanine dye and chemically sensitized with sodium p-toluenethiosulfonate, sodium p-toluenesulfinate and benzothiazolecarbazole. At the end of the chemical digestion, non-deionized gelatin (having a viscosity at 60°C in water at 6.67% w/w of 5.5 mPas, a conductivity at 40°C in water at 6.67% w/w of 1,100  $\mu$ S/cm and 4,500 ppm of Ca<sup>++</sup>) was added to the emulsion in an amount to have 83% by weight of deionized gelatin and 17% by weight of non-deionized gelatin. The emulsion, containing 5-methyl-7-hydroxy-triazaindolizine stabilizer and a hardener, was divided into twelve portions. Each portion was coated on each side of a blue polyester film support at a silver coverage of 2.15 g/m<sup>2</sup> and a gelatin coverage of 1.5 g/m<sup>2</sup> per side. A non-deionized gelatin protective supercoat containing 1.01 g/m<sup>2</sup> of gelatin per side and the compounds indicated in Table 1 was applied on each coating so obtaining seventeen different double-side radiographic films 1 to 17.

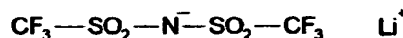
TABLE 1

Sample	Triton™ X-100 mg/m <sup>2</sup>	Triton™ X-200 mg/m <sup>2</sup>	Zonyl™ FSN mg/m <sup>2</sup>	Compound A mg/m <sup>2</sup>	Compound B mg/m <sup>2</sup>	Compound C mg/m <sup>2</sup>	Note
1	50	105					control
2	50	70					control
3	50	105		40			control
4	50	105			40		control
5	50	105	40				control
6	50	105				40	control
7	50	105		70			control
8	50	105			70		control
9	50	105	40		40		invention
10	50	105			40	40	invention
11	50	70	40	40			invention
12	50	70	40		40		invention
13	50	70			40	40	invention
14	50	40			40	70	invention
15	50	10			40	80	invention
16	50	105			20	40	invention
17	50	105			10	40	invention

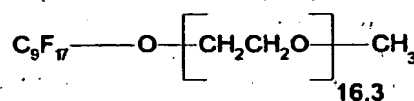
Compound A is a perfluoromethylsulfonylmethide lithium salt having the following formula:



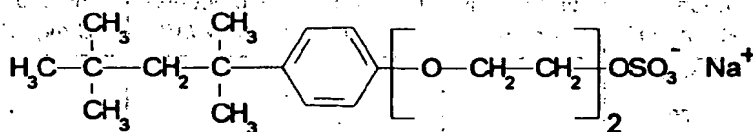
compound B is a perfluoromethylsulfonylimide lithium salt having the following formula:



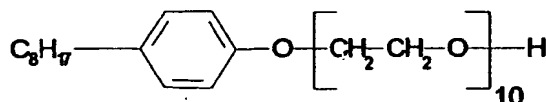
compound C is a non-ionic perfluoroalkylenepolyoxyethylene surfactant having the following formula:



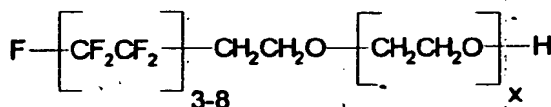
Triton™ X-200 is the trade name of an anionic surfactant of the alkylphenoxyethylene sulfonate type having the following formula:



Triton™ X-100 is the trade name of a non-ionic surfactant of the alkylphenoxyethylene type having the following formula:



Zonyl™ FSN is the trade name of a non-ionic surfactant of the perfluoroalkylpolyoxyethylene type, manufactured by DuPont and having the following formula:



wherein x is an integer from 10 to 20.

The samples 1 to 17 were conditioned for 160 minutes at 70°C and 40% of relative humidity to evaluate the sensitometric properties, and for 15 hours at 50°C and 20% relative humidity to evaluate the physical properties. After conditioning, the samples were exposed and developed. The samples were then evaluated according to the following tests.

## CHARGE DECAY TIME TEST

According to this test, the static charge dissipation of each of the films was measured. The films were cut into 45x54mm samples and conditioned at 25% relative humidity and T=21°C for 15 hours. The charge decay time was measured with a Charge Decay Test Unit JCI 155 (manufactured by John Chubb Ltd., London). This apparatus deposits a charge on the surface of the film by a high voltage corona discharge and a fieldmeter allows observation of the decay time of the surface voltage. The lower the time, the better the antistatic properties of the film. To prevent the charge decay behavior of the tested surface from being influenced by the opposite surface, this surface was grounded by contacting it with a metallic back surface.

## SURFACE RESISTIVITY TEST

According to this test the resistivity of the sample surface was measured using the Hewlett Packard model 4329A high resistance meter. The lower the value, the better the antistatic protection of the film.

## SLIPPERINESS TEST

This test was performed with a Lhomargy apparatus. It consists of a slide moving on the film at a speed of about 15 cm/min. A force transducer connected to the slide transforms the applied force into an amplified DC voltage which is recorded on a paper recorder. The force applied to start the sliding movement represents the value of static slipperiness. The movement of the slide on the film is not continuous. The discontinuity of the movement can be measured (in terms of slipperiness difference) from the graph of the paper recorder. This value represents the dynamic slipperiness. It was noted that the more the movement was discontinuous (i.e., the higher the value of slipperiness difference), the better was the performance of the film.

The results of the above mentioned tests are summarized in the following Table 2.

TABLE 2

Physical properties					
Sample	Decay Time (sec)	Surface Resistivity ( $\Omega/\text{cm}^2$ )	Static Slipperiness	Dynamic Slipperiness	NOTE
1	184	$9.4 \cdot 10^{12}$	130	114	Control
2	215	$9.8 \cdot 10^{12}$	138	116	Control
3	234	$1.0 \cdot 10^{13}$	124	95	Control
4	319	$1.3 \cdot 10^{13}$	150	120	Control
5	108	$4.1 \cdot 10^{12}$	144	90	Control
6	105	$6.0 \cdot 10^{12}$	112	86	Control
7	487	$1.6 \cdot 10^{13}$	103	92	Control
8	437	$1.5 \cdot 10^{13}$	118	111	Control
9	49	$2.8 \cdot 10^{12}$	142	85	Invention
10	12	$7.9 \cdot 10^{11}$	130	96	Invention
11	130	$5.4 \cdot 10^{12}$	97	75	Invention
12	55	$3.6 \cdot 10^{12}$	102	68	Invention
13	28	$1.7 \cdot 10^{12}$	137	95	Invention
14	25	$1.1 \cdot 10^{12}$	138	107	Invention
15	38	$1.9 \cdot 10^{12}$	137	107	Invention
16	14	$8.1 \cdot 10^{11}$	142	98	Invention
17	14	$8.2 \cdot 10^{11}$	129	98	Invention

Samples 9 to 17 of the invention give the best results in terms of decay time and surface resistivity. In particular, samples 16 and 17 comprising compound C and compound B give the best results.

In the following Table 3 are summarized the sensitometric characteristics of samples 1 to 17. The presence of the antistatic layer of the present invention does not adversely affect the good sensitometric characteristics of the silver halide materials.

TABLE 3

Sensitometry					
Sample	D.min	D.max	Speed	Contrast	NOTE
1	0.15	1.53	2.55	1.41	Control
2	0.15	1.61	2.51	1.46	Control
3	0.15	1.55	2.51	1.45	Control
4	0.15	1.65	2.51	1.45	Control
5	0.15	1.66	2.51	1.49	Control
6	0.15	1.62	2.46	1.59	Control
7	0.15	1.58	2.52	1.46	Control
8	0.15	1.53	2.56	1.43	Control
9	0.15	1.66	2.49	1.48	Invention
10	0.15	1.58	2.55	1.41	Invention
11	0.15	1.58	2.57	1.49	Invention
12	0.15	1.52	2.57	1.41	Invention
13	0.15	1.56	2.54	1.45	Invention
14	0.16	1.57	2.52	1.44	Invention
15	0.16	1.52	2.52	1.34	Invention
16	0.16	1.55	2.54	1.49	Invention
17	0.16	1.49	2.58	1.34	Invention

## EXAMPLE 2

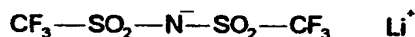
A tabular grain silver bromide emulsion (having an average diameter:thickness ratio of about 7.6:1, prepared in the presence of a deionized gelatin having a viscosity at 60°C in water at 6.67% w/w of 4.6 mPas, a conductivity at 40°C in water at 6.67% w/w of less than 150  $\mu$ S/cm and less than 50 ppm of Ca<sup>++</sup>) was optically sensitized to green light with a cyanine dye and chemically sensitized with sodium p-toluenethiosulfonate, sodium p-toluene-sulfinate and benzothiazoleiodoethylate. At the end of the chemical digestion, non-deionized gelatin (having a viscosity at 60°C in water at 6.67% w/w of 5.5 mPas, a conductivity at 40°C in water at 6.67% w/w of 1,100  $\mu$ S/cm and 4,500 ppm of Ca<sup>++</sup>) was added to the emulsion in an amount to have 83% by weight of deionized gelatin and 17% by weight of non-deionized gelatin. The emulsion, containing 5-methyl-7-hydroxy-triazaindozine stabilizer and a hardener, was divided into twelve portions. Each portion was coated on each side of a blue polyester film support at a silver coverage of 2.15 g/m<sup>2</sup> and a gelatin coverage of 1.5 g/m<sup>2</sup> per side. A non-deionized gelatin protective supercoat containing 1.01 g/m<sup>2</sup> of gelatin per side, 16mg/m<sup>2</sup> of Tergitol™ 4 as coating aid, and the compounds indicated in Table 4 was applied on each coating so obtaining twelve different double-side radiographic films 1 to 9. Tergitol™ 4 is the trade name of an alkylsulfate surfactant manu-

factured by Union Carbide.

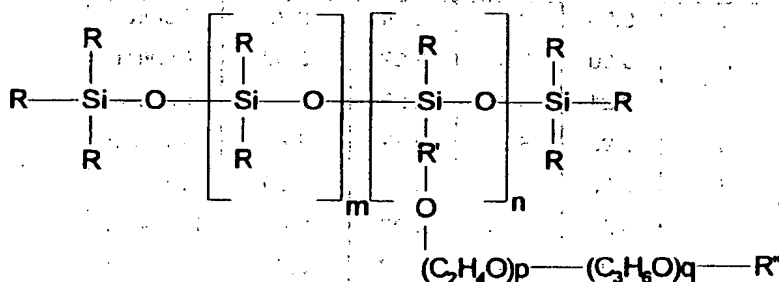
TABLE 4

Sample	Compound 1 mg/m <sup>2</sup>	Zonyl™ FSN mg/m <sup>2</sup>	Silwet™ L-7605 mg/m <sup>2</sup>	NOTE
1	13	/	/	Control
2	/	52	/	Control
3	/	/	20	Control
4	13	52	/	Invention
5	13	/	39	Invention
6	13	52	39	Invention
7	13	52	20	Invention
8	13	52	7	Invention
9	26	90	39	Invention

compound 1 is a perfluoromethylsulfonylimide lithium salt having the following formula:



Silwet™ L-7605 is the trade name of a polyalkyleneoxide-modified dimethylpolysiloxane-surfactant manufactured by Union Carbide and having the following formula:



wherein m ranges from 5 to 100, n ranges from 2 to 50, p ranges from 5 to 50, and q ranges from 0 to 50.

The samples 1 to 9 were conditioned for 160 minutes at 70°C and 40% of relative humidity to evaluate the sensitometric properties, and for 15 hours at 50°C and 20% relative humidity to evaluate the physical properties. After conditioning the samples were exposed and developed. The samples were then evaluated according to the same tests of Example 1.



The results of the tests are summarized in the following Table 5.

TABLE 5

Physical properties					
Sample	Decay Time (sec)	Surface Resistivity ( $\Omega/\text{cm}^2$ )	Static Slipperiness	Dynamic Slipperiness	NOTE
1	104	$5.83 \cdot 10^{12}$	102	80	Control
2	81	$3.62 \cdot 10^{12}$	84	50	Control
3	137	$5.93 \cdot 10^{12}$	107	86	Control
4	46	$2.21 \cdot 10^{12}$	78	47	Invention
5	48	$3.6 \cdot 10^{12}$	81	63	Invention
6	25	$1.44 \cdot 10^{12}$	78	50	Invention
7	24	$1.26 \cdot 10^{12}$	73	51	Invention
8	26	$1.41 \cdot 10^{12}$	74	44	Invention
9	10	$3.40 \cdot 10^{11}$	62	42	Invention

The combination of the present invention gives a strong improvement in all the antistatic characteristics of the photographic material, without adversely affect the sensitometric results, as showed in the following table 6.

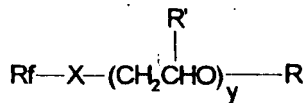
TABLE 6

Sensitometry					
Sample	D.min	D.max	Speed	Contrast	NOTE
1	0.20	3.62	2.24	2.73	Control
2	0.20	3.61	2.27	2.67	Control
3	0.21	3.67	2.27	2.70	Control
4	0.20	3.65	2.27	2.61	Invention
5	0.20	3.66	2.28	2.60	Invention
6	0.20	3.51	2.29	2.42	Invention
7	0.20	3.68	2.27	2.71	Invention
8	0.20	3.66	2.27	2.61	Invention
9	0.20	3.88	2.25	2.63	Invention

### Claims

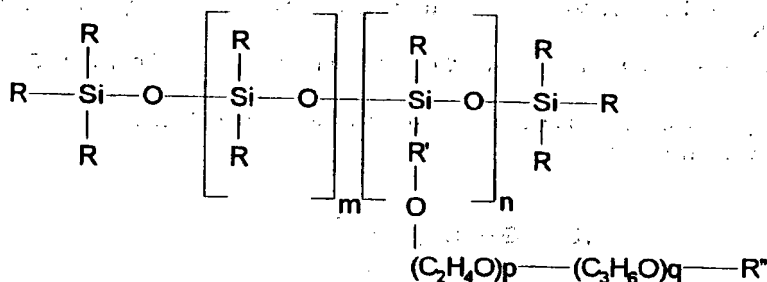
1. A silver halide photographic material comprising a support, at least one silver halide emulsion layer coated thereon, and a hydrophilic colloid layer coated over said at least one silver halide emulsion layer, wherein said hydrophilic colloid layer comprises a combination of (a) at least one surfactant selected from the group consisting of non-ionic perfluoroalkyl(ene)poly-oxyethylene surfactants and polyoxyethylene-modified polysiloxane surfactants, and (b) at least one salt selected from the group of salts of perfluoroalkylsulfonyl imides and perfluoroalkylsulfonyl methides.
2. The silver halide photographic material of claim 1, characterized in that said hydrophilic colloid layer further comprises at least one surfactant selected from the group consisting of (a) non-ionic polyoxyethylene surfactants, (b) anionic polyoxyethylene surfactants, and (c) alkylsulfate surfactants.

3. The silver halide photographic material according to claim 1 or 2 characterized in that said non-ionic perfluoro-alkyl(ene)polyoxyethylene surfactant is represented by the following formula:



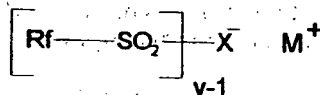
wherein Rf can be a perfluoroalkyl group, a perfluoroalkylene group, a perfluorocycloalkyl group, and a perfluorocycloalkylene group having from 4 to 16 carbon atoms, X can be -O-, -SO<sub>2</sub>NR<sup>-</sup>-, -CONR<sup>-</sup>-, -CH<sub>2</sub>O-, or a single bond, R, R' and R'' are, independently, hydrogen or a lower alkyl of from 1 to 4 carbon atoms, and y is a number from 6 to 30.

4. The silver halide photographic material according to claim 1 or 2 characterized in that said polyoxyethylene modified-polysiloxane surfactant is represented by the following formula:



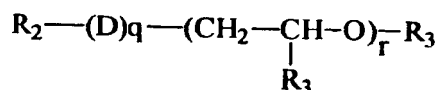
wherein R is a lower alkyl having from 1 to 4 carbon atoms, R' is a lower alkylene having from 1 to 4 carbon atoms, R'' is hydrogen or a lower alkyl of from 1 to 4 carbon atoms, m is an integer from 5 to 100, n is an integer from 2 to 50, p is an integer from 5 to 50, and q is an integer from 0 to 50.

5. The silver halide photographic material according to claim 1 or 2 characterized in that said salt of perfluoroalkylsulfonyl imide or perfluoro-alkylsulfonyl methide is represented by the following formula:



wherein Rf is a fluorinated alkyl group having 1 to 10 carbon atoms, X is nitrogen or carbon atom, M is an organic or inorganic cation, and v is the X valence, and wherein two Rf groups can join together to form a ring.

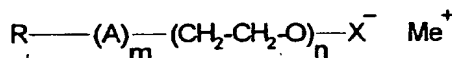
6. The silver halide photographic material according to claim 5 characterized in that M is selected from the group consisting of alkali metal cations, alkaline-earth metal cations, alkylammonium, and quaternary ammonium cations.
7. The silver halide photographic material according to claim 5 characterized in that M is a lithium cation.
8. The silver halide photographic material according to claim 2 characterized in that said non-ionic polyoxyethylene surfactant is represented by the following formula:



wherein R<sub>2</sub> represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 1 to 30 carbon atoms

or an aryl group having 6 to 30 ring atoms or a combination thereof,  $R_3$  represents a hydrogen atom or a methyl group, D represents a group  $-O-$ ,  $-S-$ ,  $-\text{COO}-$ ,  $-\text{NR}_4-$ ,  $-\text{CO-NR}_4-$ , or  $-\text{SO}_2-\text{NR}_4-$ , wherein  $R_4$  represents a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, q represents 0 or 1 and r represents an integer of 2 to 50.

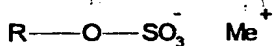
9. The silver halide photographic material according to claim 2 characterized in that said anionic polyoxyethylene surfactant is represented by the following formula:



wherein R is an aliphatic, aromatic or a mixed hydrocarbon residue and preferably a linear or branched alkyl group having from 4 to 18 carbon atoms or an aryl group substituted with one or more alkyl groups altogether having from 4 to 18 carbon atoms, A is a divalent organic residue, preferably a carbonyl, a sulfonyl, an amino or an alkylene group preferably having from 1 to 3 carbon atoms, an oxygen atom or groups consisting of two or more of the above-mentioned groups, such as for example carbonylamino, sulfonylamino, aminocarbonyl, aminosulfonyl, or ester, X is an anionic group selected from the class consisting of sulfonate group, carboxylate group, phosphate group and sulfate group,

Me is an alkali or alkaline-earth metal, and m is 0 or 1 and n is an integer of from 1 to 25.

10. The silver halide photographic material according to claim 2 characterized in that said alkylsulfate surfactant is represented by the following formula:



wherein R is a linear or branched alkyl group having from 4 to 18 carbon atoms, and Me is an alkali metal.

11. The silver halide photographic material according to claim 1 or 2 characterized in that said salt of perfluoroalkylsulfonyl imide or perfluoro-alkylsulfonyl methide is present in an amount of from 1 to 100 mg/m<sup>2</sup> of top-coat protective layer.
12. The silver halide photographic material according to claim 1 or 2 characterized in that said non-ionic perfluoro-alkyl(ene)polyoxyethylene surfactant is present in an amount of from 10 to 100 mg/m<sup>2</sup> of top-coat protective layer.
13. The silver halide photographic material according to claim 1 or 2 characterized in that said polyoxyethylene-modified polysiloxane surfactants is present in an amount of from 1 to 100 mg/m<sup>2</sup> of top-coat protective layer.
14. The silver halide photographic material according to claim 2 characterized in that each of said surfactants selected from the group consisting of non-ionic polyoxyethylene surfactants, anionic polyoxyethylene surfactants, and alkyl-sulfate surfactants are present in an amount of from 10 to 200 mg/m<sup>2</sup> of top-coat protective layer.
15. A silver halide photographic material comprising a support, at least one silver halide emulsion layer coated thereon, and a hydrophilic colloid layer coated on said at least one silver halide emulsion layer, wherein said hydrophilic colloid layer comprises a combination of (a) a non-ionic perfluoroalkyl(ene)poly-oxyethylene surfactants, (b) a polyoxyethylene-modified polysiloxane surfac-tants, and (c) at least one salt selected in the group of salts of perfluoro-alkylsulfonyl imide and perfluoroalkylsulfonyl methide.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 95 10 9067

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.6)
Y	EP-A-0 242 853 (KONISHIROKU PHOTO-INDUSTRY CO. LTD.) * compounds S-3, S-7, F-16, F-17 * * page 30, line 24 - page 33; claims 1, 3, 5, 6 * * page 91, line 22 - page 92, line 2 *	1-13	G03C1/38 G03C1/89
Y	US-A-4 370 254 (K-H MITSCHKE ET AL) * column 3, line 20 - line 23; claim 2 *	1-13	
D, A	US-A-4 505 997 (M B ARMAND ET AL) * claims 1-5, 9 *	1, 5	
A	EP-A-0 111 338 (E.I. DU PONT DE NEMOURS AND CO.) * Table 1, tests 12-20 * * page 7, line 17 - line 31 *	1-3	
			TECHNICAL FIELDS SEARCHED (Int. CL.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 October 1995	Examiner Bolger, W
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (3.12.94) (P04C01)

# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>56612W0004</b>	<b>FOR FURTHER ACTION</b> <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. <b>PCT/US 02/ 13002</b>	International filing date (day/month/year) <b>22/04/2002</b>	(Earliest) Priority Date (day/month/year) <b>10/05/2001</b>
Applicant  <b>3M INNOVATIVE PROPERTIES COMPANY</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 02 sheets.  
☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/13002

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K3/16 G03C1/85 G03C1/89

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01 25326 A (3M INNOVATIVE PROPERTIES CY) 12 April 2001 (2001-04-12) claims 1,3,8-18	1-36
A	EP 0 690 338 A (MMM) 1 March 1996 (1996-03-01) claims 1-3,5-15	1-36
A	US 5 362 613 A (K SHIRATSUCHI) 8 November 1994 (1994-11-08) claim 1	1-36
A	EP 0 650 088 A (KODAK) 26 April 1995 (1995-04-26) page 3, line 6 -page 4, line 35; claims 1-6,8-11	1-36

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

15 July 2002

Date of mailing of the international search report

24/07/2002

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Vanhecke, H

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/13002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0125326	A	12-04-2001	US 6372829 B1 AU 3743500 A WO 0125326 A1	16-04-2002 10-05-2001 12-04-2001
EP 690338	A	03-01-1996	EP 0690338 A1 JP 8015823 A US 5541049 A	03-01-1996 19-01-1996 30-07-1996
US 5362613	A	08-11-1994	JP 2779724 B2 JP 5194671 A	23-07-1998 03-08-1993
EP 650088	A	26-04-1995	EP 0650088 A2 JP 7233365 A US 5744295 A	26-04-1995 05-09-1995 28-04-1998

